



Degradation of atrazine using metalloporphyrins supported on TiO₂ under visible light irradiation

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ABSTRACT

The photocatalytic activity of tetra(4-carboxyphenyl)porphyrin with different metal centers (Fe(III), Cu(II), Zn(II) and metal-free), adsorbed on TiO₂ surface has been investigated by carrying out the photodegradation of atrazine in aqueous solution and under visible light irradiation. Under this condition, no photocatalytic activity was found meaning that anion superoxide (which was evidenced by photodegradation of luminol) is not sufficiently oxidant to degrade atrazine. However by adding hydrogen peroxide in the solution, a degradation of atrazine was observed. Under this condition, the maximum photocatalytic activity was obtained using Cu(II) porphyrin as photosensitizer (82% of degradation after 1 h of irradiation). The influence of H₂O₂ concentration has been studied. It has been found that in the range 0.015–0.05 mol L⁻¹ the higher the concentration the higher the rate of degradation, whereas for higher H₂O₂ concentrations, the rate of degradation leveled off. Intermediate products were identified using high performance liquid chromatography-Diode Array Detector (HPLC-DAD) and GC-MS and a mechanism of degradation was proposed.

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1. Introduction

Photocatalysis is a promising method for the treatment and purification of polluted water [1,2]. The efficiency of this system is based on the production of reactive species, such as holes (h⁺), hydroxyl radicals (*OH), superoxide anions (O₂^{•-}) which are able to oxidize and mineralise almost all organic pollutants yielding CO₂ and inorganic ions as final products. The photo-assisted catalysis involves the irradiation of a semiconductor like TiO₂ with UV light at wavelength below 387 nm, generating electron-hole pair on the catalyst surface and inducing the formation of radicals. Different kinds of photocatalysts have been proposed in the literature, including SnO₂, TiO₂, CdS, and In₂O₃ [3–6], but it is generally well admitted that only TiO₂ gives the best results. Unfortunately, the wavelengths required for initiating the photocatalytic process represent only 5% (the fringe comprised between 300 nm and 400 nm) of the ones coming from sunlight. In spite of the fact that the process is rather simple, that the cost is low and that it represents an ecological character, only few environmental applications have emerged.

To overcome this problem, different approaches have been proposed in the literature in which the response of the semiconductor was extended towards the visible region. Among them, dye-sensitized TiO₂ has been widely used either with dyes present in solution or grafted on TiO₂ [7]. In this case, photosensitization is produced by a photoinduced electron transfer, from the excited dye to the conduction band (CB) of TiO₂ [8–10]. While electrons CB (e_{CB}) react with acceptor molecules (i.e., with molecular oxygen forming O₂^{•-}), the valence band (VB) remains unaffected [11,12].

Nature accomplishes enhanced light absorption by stacking chlorophyll-containing thylakoid membranes of the chloroplast to form the grana structures that act as light-harvesting antenna. These absorb the incident light and then channel the excitation energy to reaction centers, where light-induced charge separation takes place [13]. Given their primary role in photosynthesis, the use of porphyrins (Ps) as light harvesters on TiO₂ is particularly attractive. They have a delocalized macrocyclic structure, very strong absorption in the visible region and their excited states energy favor electron transfer to the TiO₂ conduction band. Furthermore, porphyrins offer a wide variety of photochemical and redox properties which can be easily tuned by peripheral substituent modifications or metal complexation [14–18].

Charge transfer from the sensitizer induces an oxidized porphyrin (P⁺) which can be reduced to P by water molecules acting as electron donors. The reported half-wave potentials of the

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P^+/P couple for several metalloporphyrins are in the range 0.95–1.19V_{NHE}, while the standard reduction potential of the O_2/H_2O couple is 1.23V_{NHE} [19], then, P^+ regeneration by H_2O molecules is thermodynamically allowed [7,20,21].

In this work, tetra(4-carboxyphenyl)porphyrin with different metal centers, adsorbed on TiO_2 surface (TcPPM/ TiO_2) were used as sensitizers. Atrazine was chosen as a model pollutant for studying its degradation under visible irradiation. In addition to be a model pollutant, atrazine is a selective herbicide which was used worldwide for the control of broadleaf and grassy weeds on both agricultural and nonagricultural land [22,23]. It is a common soil and water pollutant, giving rise to environmental concern due to its relatively low sorption affinity, and slow biodegradability [24,25]. Recently, its photocatalytic degradation was carried out using UV light and it was found that cyanuric acid was the final stable product [26,27]. At our knowledge, none of study of atrazine degradation in aqueous solution and under visible light irradiation has been reported. Atrazine could present a different behavior compare to more classical model pollutants such as (nitro)phenols since the reactivity of these molecules towards the reactive species involved in the photosensitization is not the same.

In addition, to better understand the origin of active oxygen species in aqueous suspensions and under visible light irradiation, we have chosen as a probe reaction the degradation of luminol, known to react with various species such as $O_2^{\bullet-}$ and $\bullet OH$ [28,29].

2. Experimental

2.1. Materials

Atrazine (purity > 98%) was acquired from Riedel-de Haën Aldrich. Methanol (high-performance liquid chromatography, HPLC, grade) was purchased from SDS (Peypin, France). Luminol sodium salt, superoxide dismutase (SOD, 4500 units/mg), mannitol and hydrogen peroxide solution (30%) were purchased from Aldrich. Other reagents were at least of analytical grade. Atrazine and luminol solutions were prepared with water from a Millipore Waters Milli-Q water purification system. TiO_2 Degussa P-25, mainly anatase, with a specific area of $50\text{ m}^2\text{ g}^{-1}$ corresponding to a particle size of ca. 30 nm was employed as support [30].

2.2. Spectroscopic measurements

The UV–vis spectra of complexes in solution were measured by using a HP 8453 spectrophotometer. The UV–vis diffuse reflectance absorption spectra of the solid complexes (free and supported on TiO_2) were measured using a Lambda 4 PerkinElmer spectrophotometer equipped with an integrating sphere. Luminol fluorescence was measured by using a Jasco FP-6505 spectrofluorometer. FT-IR spectra (KBr, photoacoustic mode) were recorded on a Bruker Tensor 27 spectrometer.

2.3. Photocatalyst preparation

Copper(II), zinc(II), iron(III) and metal-free tetra(4-carboxyphenyl)porphyrin (TcPPM) were synthesized according to the methods described in the literature [31–33]. Fig. 1 represents the porphyrin structure.

To synthesize metal-free porphyrin (TcPPH), pyrrole (30 mmol) was added to a mixture of 4-carboxybenzaldehyde (30 mmol), propionic acid (105 mL) and nitrobenzene (45 mL) with stirring at room temperature. The mixture was heated at 120°C for 1 h. After cooling and solvent removal under vacuum, porphyrin was dissolved in 250 mL of 0.1 M NaOH solution. TcPPH was precipitated with a 1 M HCl solution, filtrated, redissolved in ethanol and recrystallized by solvent evaporation.

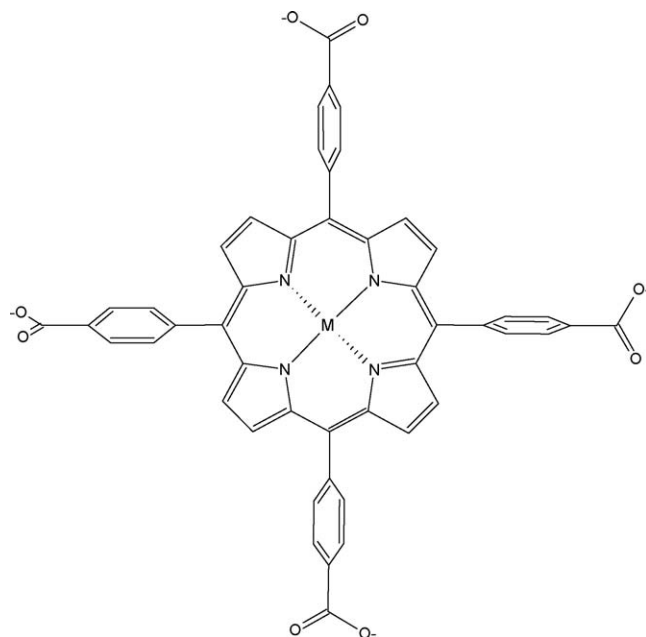


Fig. 1. Representation of porphyrin structure.

Metalloporphyrins were prepared by refluxing TcPPH (0.33 mmol) with copper(II) chloride decahydrate, zinc(II) acetate or iron(III) chloride heptahydrate (amounts corresponding to 1.82 mmol) in N,N' -dimethylformamide (70 mL) for 2 h. DMF was removed by distillation and TcPPM were precipitated by adding water. The precipitate was dissolved in 0.1 M NaOH solution and reprecipitated by adding 1 M HCl solution. TcPPM were dissolved in ethanol and recrystallized by solvent evaporation. Finally, porphyrins were dried at room temperature. FT-IR (KBr, cm^{-1}): 1604 s [C=C]; 1110 s, 1531 m, 1500 m, 1485 m, 1311 m, 1006 s, 1307 m [P ring]; 1701 s [C=O]; 1404 m, 1268 s [C–O] [34].

TcPPM were adsorbed on TiO_2 surface (TcPPM/ TiO_2) by adopting the procedure reported previously [35–37]: 0.25 g TiO_2 was added to 250 mL of 0.2 mM TcPPM ethanolic solution. The mixture was stirred overnight at 60°C . The solid was filtered, washed with ethanol in order to remove the unadsorbed dye and dried at room temperature. Spectral properties of porphyrins adsorbed on the surface of TiO_2 are discussed deeply in another report [20,29]. FT-IR (KBr, cm^{-1}): 1608 s [C=C]; 1535 w, 1516 w, 1469 w, 1311 w, 1054 s, [P ring]; 1384 [–COO[–]]_s; 1630 [–COO[–]]_{as} [38].

The amount of dye adsorbed on TiO_2 surface was determined by suspending 2 mg of the sample in 20 mL of 1 M NaOH solution for 2 h. An aliquot of the supernatant solution was analyzed by UV/vis spectroscopy [20].

2.4. Degradation of luminol

Experimentation on the detection of $O_2^{\bullet-}$ was carried out by suspending 0.02 g of the catalyst in 20 mL of luminol aqueous solution (2.7 μmol , pH 7). The suspension was stirred in the dark for 1 h before irradiating and O_2 was bubbled into suspension. The reaction mixture was irradiated with a Philips HPK 125 W mercury lamp and a GG395 filter (SCHOTT) was used in order to eliminate UV wavelengths. The reactions were performed at 25°C .

Sample aliquots of 0.2 mL were collected during irradiation, which were then filtered and quantified with luminol fluorescence at 430 nm (excitation wavelength was 387 nm). The concentration of luminol was calibrated from fluorescence intensity of a luminol solution of known concentration. Identifi-

Table 1UV–vis band maxima, extinction coefficients (ϵ) for metalloporphyrins free and adsorbed on TiO₂ and TiO₂ surface area covered by porphyrins percentage.

Dye	Free TcPPM				TcPPM/TiO ₂		
	Soret band		Q bands		Soret band	Q bands	Surface area covered by dye (%) ^a
	λ_{\max} (nm)	ϵ ($\times 10^3$ M ⁻¹ cm ⁻¹)	λ_{\max} (nm)	ϵ ($\times 10^3$ M ⁻¹ cm ⁻¹)	λ_{\max} (nm)	λ_{\max} (nm)	
TcPPH	416	150	513; 547	20; 8	428	521; 558	17
TcPPZn(II)	416	134	540	16	431	563	12
TcPPCu(II)	413	120	536	13	424	547	10
TcPPFe(III)	400	95	531	17	421	535	15

^a The calculated areas refer to 1 g of TiO₂. The surface area for a single porphyrin molecule was approximate to 2.25 nm²/molecule.

fication of reactive species was carried out in presence of radical scavengers: O₂^{•-} was verified by adding 3 mg of SOD to the suspension before irradiation while •OH was identified by adding 100 μ L of 0.1 M mannitol solution [28].

2.5. Photodegradation of atrazine

2.5.1. Light source

Photodegradation of atrazine was carried out in an open borosilicate (Pyrex) glass cell with an optical window of 11 cm² area equipped with a magnetic stirring bar and water circulating jacket. The irradiation spectrum was cut-off below 420 nm using a GG395 filter in order to eliminate UV wavelengths. The light source was an Osram Xenon lamp, cooled with a water circulation. The radiant flux entering the irradiation cell was determined by Reinecke salt actinometry [40,41]. The initial solution volume was 20 mL.

The reactions were carried out according to the following procedure: 0.02 g of the catalyst was added to 20 mL of atrazine solution (20 ppm). Then, the suspension was magnetically stirred in the dark for 1 h before irradiating. O₂ was bubbled into suspension and an amount of H₂O₂ was added to the suspension (0.01–0.1 M). The pH of reacting system was adjusted at 7.0 (NaOH) and the reactions were performed at 25 °C.

In the N₂-saturated experiments, the reaction solution was saturated by highly purified N₂ gas for 30–60 min. Then, the photocatalyst was dispersed through solution by magnetic stirring for 1 h before irradiating.

Atrazine degradation was carried out in presence of radical scavengers: O₂^{•-} was identified by adding 3 mg of SOD in the suspension. •OH was identified by adding 100 μ L of 0.1 M mannitol in the solution.

2.5.2. Samples preparation

During the irradiation, aliquots of the aqueous suspensions were collected at regular times and filtered through 0.45 nylon filters (Millipore) to remove catalyst particles. For HPLC-Diode Array Detectors (DADs) analysis, samples were injected directly.

GC–MS analyses of intermediate products were performed after Solid Phase Extraction (SPE) of 20 mL irradiated solution on Isolute C18 cartridges and elution with 1 mL methanol [42].

2.5.3. Analytical determinations

HPLC analyses were performed using a Shimadzu HPLC system with a DAD and a Hypersil BDS C₁₈ column (particle size 5 μ m, 125 mm length \times 4.0 mm i.d.). Mobile phase was a mixture of water and methanol, with a ratio of 45 vol.% methanol at a flow rate of 0.7 mL min⁻¹. The detection wavelength was 220 nm.

GC–MS analyses were performed on a PerkinElmer Clarus 500 system, with a capillary Elite 5MS column (length: 60 m, internal diameter: 0.25 mm, film thickness: 1.0 μ m). Injection was made at 280 °C with a split ratio of 5:1. The column temperature was held at 100 °C during 5 min, then raised at 10 °C min⁻¹ to 270 °C, and finally held at 270 °C during 30 min. Electron ionization mass

spectra were identified using NIST 2002 Library and most of these compounds were identified by using the NIST library program with a fit higher than 90%.

3. Results

3.1. Absorption spectra

Table 1 shows the UV–vis absorption band maxima of metal-free, Fe(III), Cu(II), Zn(II) porphyrins. For TcPPH, the strong Soret band appears at 416 nm arising from the transition of a_{1u}(π)–e_g^{*}(π), and the less intense Q bands in the 515–600 nm region corresponding to the a_{2u}(π)–e_g^{*}(π) transition. Compared to TcPPH and TcPPZn (or regular porphyrins), the absorption bands of Fe and Cu porphyrins present a blue shift [43,44].

The absorption spectra of porphyrins adsorbed onto TiO₂ particles are similar to those of the corresponding free porphyrins spectra but exhibit a small red shift due to the interaction of the anchoring groups with the surface (Fig. 2) [15,45].

The amount of TcPPM adsorbed onto TiO₂ was found to be ~ 4 –6 μ mol g⁻¹. Using an available surface area of ca. 50 m² g⁻¹ for TiO₂ and assuming that a TcPPM molecule lying in a flat geometry would occupy an area of about 2.3 nm², the percentage of TiO₂ surface area covered by TcPPM molecules is calculated to be $\sim 17\%$ (Table 1) [30].

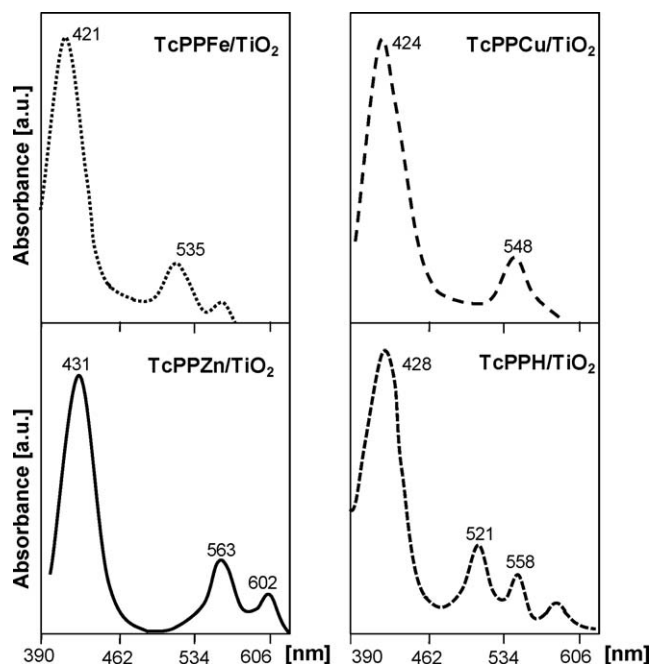


Fig. 2. UV–vis diffuse reflectance spectra of Fe, Cu, Zn and metal-free porphyrins adsorbed on TiO₂ surface.

3.2. Identification of the main active species generated during the degradation of luminol

Oxygen plays an important role in photocatalytic reactions induced by visible light either by scavenging e_{CB} to effectively prevent the recombination between e_{CB} and P^+ , or as the predominant reactant able to generate active species, such as superoxide anions [46]. For example, ESR signal of $O_2^{\bullet-}$ generated by porphyrin-sensitized TiO_2 suspensions has been reported, which was strongly restricted by adding superoxide dismutase into suspension [47].

According to previous studies, the luminol photocatalytic oxidation is carried out by $O_2^{\bullet-}$ or OH^\bullet [28,29,39]. Fig. 3 shows the degradation of luminol with visible light irradiation by using TiO_2 , TcPPCu/ TiO_2 in presence of molecular oxygen. It is clearly shown that no degradation of luminol was obtained with pure TiO_2 confirming the fact that TiO_2 alone is not able to initiate photoreaction under visible light. TcPPCu/ TiO_2 shows a degradation of luminol around 60%. The species formed can be evidenced by investigating the effect of SOD (a scavenger of $O_2^{\bullet-}$ [48,49]) and mannitol (a scavenger of OH^\bullet [28]) on luminol degradation. The addition of SOD, which reacts with superoxide radical anions, but not hydroxyl radicals [50], affected dramatically the degradation of luminol. By contrast, the reaction was not significantly changed when mannitol was added in the solution. These results indicate that mainly $O_2^{\bullet-}$ is formed in the present reacting system.

3.3. Degradation of atrazine

In order to study the adsorption of atrazine, a pesticide solution (20 ppm, 0.1 mmol L^{-1}) was magnetically stirred in the dark for 60 min in presence of i.e. TcPPCu/ TiO_2 ; the adsorption equilibrium was rapidly reached (within 15 min) and only 3% of atrazine was adsorbed after 60 min on TiO_2 surface corresponding to a surface coverage of less than $0.1 \text{ molecule nm}^{-2}$. This represents a low adsorbed organic molecule. As a consequence for the following experiments, the atrazine solutions were magnetically stirred in the dark during 60 min before irradiating to make sure that adsorption equilibrium was reached.

Fig. 4 shows the photodegradation of atrazine under different experimental conditions using i.e. TcPPCu/ TiO_2 as catalyst and $I_0 = 1.1 \times 10^{-4} \text{ Einstein L}^{-1} \text{ s}^{-1}$ ($\lambda > 420 \text{ nm}$). The figure shows clearly that no degradation of atrazine was obtained in presence of molecular oxygen indicating that $O_2^{\bullet-}$ by itself cannot interact directly with atrazine. This result differs strongly from the one obtained with i.e. nitrophenol for which a degradation took place

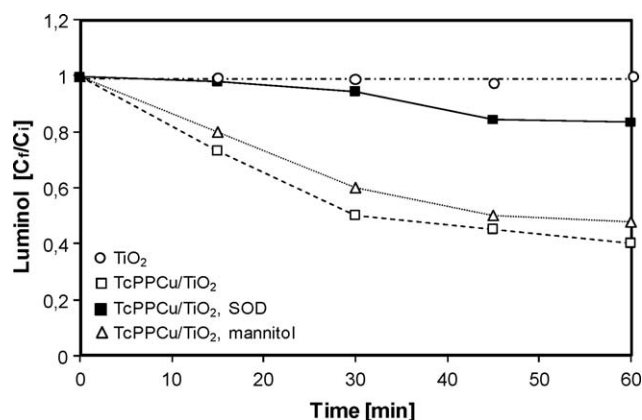


Fig. 3. Degradation of luminol as a function of irradiation time in presence of TcPPCu/ TiO_2 and O_2 . Experimental conditions: luminol = $2.7 \mu\text{mol}$; catalyst charge = 1 g L^{-1} ; reaction volume of 20 mL ; $T = 25^\circ \text{C}$, $\lambda > 420 \text{ nm}$.

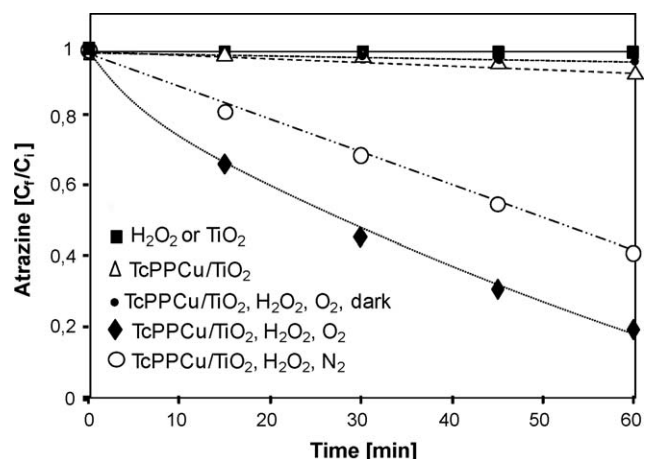
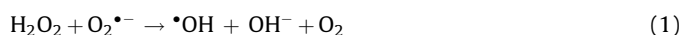


Fig. 4. Degradation of atrazine as a function of irradiation time in presence of TcPPCu/ TiO_2 , O_2 and H_2O_2 . Experimental conditions: [atrazine] = 20 ppm ; $[H_2O_2] = 0.05 \text{ M}$; catalyst charge = 1 g L^{-1} ; reaction volume = 20 mL ; $I_0 = 1.1 \times 10^{-4} \text{ Einstein L}^{-1} \text{ s}^{-1}$; $\lambda > 420 \text{ nm}$.

[51,52]. It means that such treatment cannot be applied directly for all kind of organic pollutants just like hydroxyl radicals are unable to degrade, for example cyanuric acid or chlorofluorocarbons. Several works have reported that atrazine degradation is initiated by OH^\bullet , which is a better oxidant (its reducing potential is 2.07 V at $\text{pH } 7$ compared to 0.25 V for $O_2^{\bullet-}$) and more reactive than superoxide anions [53].

The following reactions show that H_2O_2 can be reduced either by $O_2^{\bullet-}$ or by e_{CB} to yield OH^\bullet [54,55]:



Hence, to degrade atrazine using photosensitizers and visible light irradiation, hydrogen peroxide was added to the aqueous suspensions (hydrogen peroxide is used in the photo-Fenton process but with UV light irradiation). Under this condition, Fig. 4 shows that 82% of degradation was obtained after 1 h of irradiation while no degradation of atrazine was observed using either pure TiO_2 or H_2O_2 confirming the fact that neither TiO_2 nor H_2O_2 by themselves are able to initiate photodegradation under visible light irradiation. We also observe that in the dark, a degradation of atrazine with added H_2O_2 occurs, but the kinetic remains slow

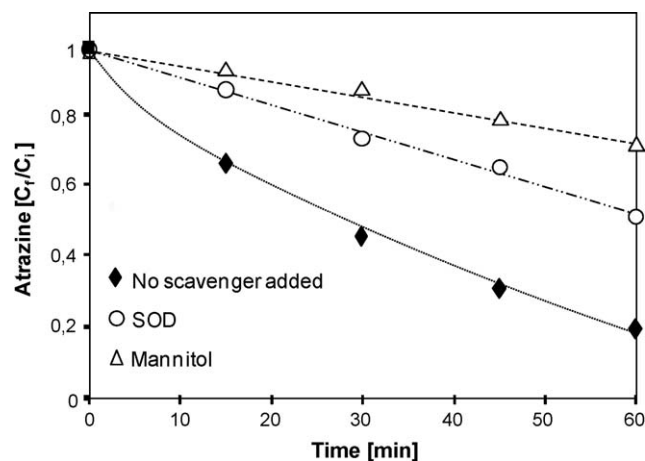


Fig. 5. Degradation of atrazine as a function of irradiation time by using TcPPCu/ TiO_2 , O_2 and H_2O_2 ; in presence of SOD and mannitol. Other experimental conditions as in Fig. 4.

Table 2

Identification by GC–MS of photoproducts of atrazine.

Compound	Name	R_t^a (min)	Mass spectrum ^b (m/z)
I	2-Chloro-4-(ethylamino)-6-(isopropylamine)-triazine	29.4	215
II	2-Chloro-4-acetamido-6-isopropylamine-1,3,5-triazine	31.8	229
III	2-Chloro-4-amido-6-isopropylamine-1,3,5-triazine	30.3	
IV	2-Chloro-4-ethylamino-6-(2-propanol)amino-1,3,5-triazine	Not identified	
V	Desethylatrazine	27.2	187
VI	Edisopropylatrazine	27	173
VII	Desethyl-desisopropyl atrazine	24.6	

^a Retention time.^b MS analysis.

since only less than 5% of the substrate is oxidized after 1 h of reaction.

To assess the role of dissolved O_2 during the photocatalytic degradation process, N_2 was bubbled through the suspension to remove O_2 from the solution. In this condition (TcPPCu/TiO₂–H₂O₂–N₂), a decrease of ca. 22% of the degradation (Fig. 4) occurred compared to TcPPCu/TiO₂–H₂O₂–O₂, confirming the importance of O_2 to produce $\bullet OH$.

To better understand the role played by $O_2^{\bullet -}$ and $\bullet OH$ on atrazine degradation, SOD and mannitol were added to TcPPCu/TiO₂ aqueous dispersion (Fig. 5). Both SOD and mannitol affected the photoreaction: the atrazine degradation decreased to 20% with SOD and 63% with mannitol (compared to the control reactions). These results suggest that $\bullet OH$ are predominantly formed in the reaction system and $O_2^{\bullet -}$ could be a precursor of $\bullet OH$.

3.4. Effect of H₂O₂ concentration on the rate of degradation

Hydrogen peroxide might be considered as the limiting reagent in the atrazine degradation process. Initially, it could be expected that an increase of H₂O₂ led to an increase of $\bullet OH$ radicals available to attack more efficiently atrazine. In the present case, for H₂O₂ concentration range 0.015–0.05 M the more the H₂O₂ the more the atrazine degradation. However, for higher H₂O₂ concentrations, the percent of atrazine degradation levels off which can be attributed to other side reactions occurring simultaneously (Fig. 6). For example, reactions (3) and (4) show that H₂O₂ may react with hydroxyl radical to form peroxy radical (HO₂ \bullet), which is a much weaker oxidant than hydroxyl radical [56]. As a result, the reaction may be inhibited by an over dose of H₂O₂.



3.5. Reaction pathway

The atrazine oxidation under visible light irradiation, in presence of hydrogen peroxide, molecular oxygen and TcPPCu/TiO₂ was studied in order to observe the role of hydroxyl radicals as the main oxidant generated [57] and to determine the pathways of atrazine degradation.

After only 1 h of visible light irradiation, 82% of atrazine was phototransformed. As shown in Fig. 7, intermediates and the degradation pathway involve and confirm the presence of hydroxyl radicals. Indeed, atrazine degradation seems to be initiated by $\bullet OH$ attacks on the aminoalkyl groups of the side chains generating free organic radicals by a very fast hydrogen atom abstraction from organic substrate. After that, an alkyl oxidation takes place forming intermediates II–III–IV, which is followed by a dealkylation to give V–VI–VII compounds. Although intermediate IV was not identified, it has been suggested like a precursor of VI [58]. The detection of intermediate VII suggests that

the oxidation at the carbon atoms adjacent to the amino groups is carried out in the early part of atrazine degradation.

No photoproducts from dehalogenation by electron transfer were observed, confirming that atrazine oxidation was realized mainly by $\bullet OH$ (Table 2).

The scheme of reaction proposed (Fig. 7) is consistent with previous studies realized with TiO₂ and UV light and Fenton-like reactions, which lead to production of $\bullet OH$ [56,57]. Pelizzetti et al. [58] have shown that under long time irradiation, the hydrolysis of the atom of chlorine and the further displacement of the amino groups by hydroxyl groups lead to the formation of cyanuric acid as final stable organic product of degradation.

3.6. Degradation of atrazine by metalloporphyrins adsorbed on TiO₂ surface

The photocatalytic activity of four phenylporphyrins, namely, TcPPCu, TcPPFe, TcPPZn and TcPPH, adsorbed on TiO₂, was studied in atrazine degradation, in presence of H₂O₂ and O₂ (Fig. 8). After 1 h of irradiation, the most active catalysts were TcPPCu, TcPPFe with 82 and 57% of degradation, respectively; while for TcPPZn and TcPPH 40 and 25%, respectively, was observed. These results indicate that metal ion plays an important role in the photoreactivity.

In general, we observed that complexes like TcPPFe and TcPPCu containing a central metal ion with unfilled d orbitals show higher photocatalytic activity. By contrast, those containing a metal ion with filled electron shells or metal-free complexes manifest lower photoreactivity. Recently, the paramagnetic properties of Fe(III) and Cu(II) complexes adsorbed on TiO₂ surface were evidenced by EPR spectroscopy [59].

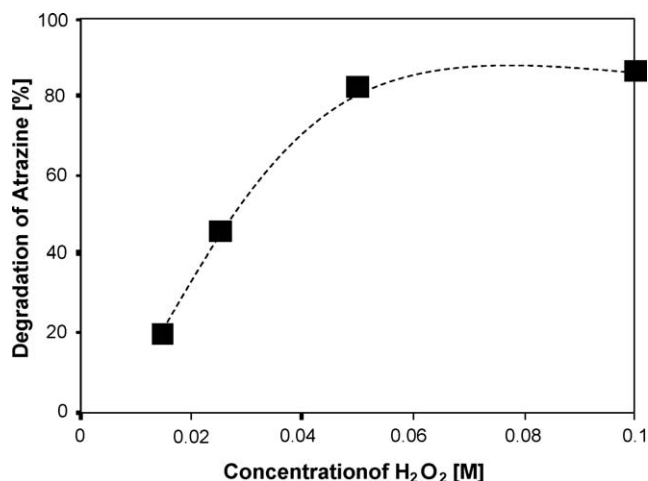


Fig. 6. H₂O₂ concentration effect on atrazine degradation.

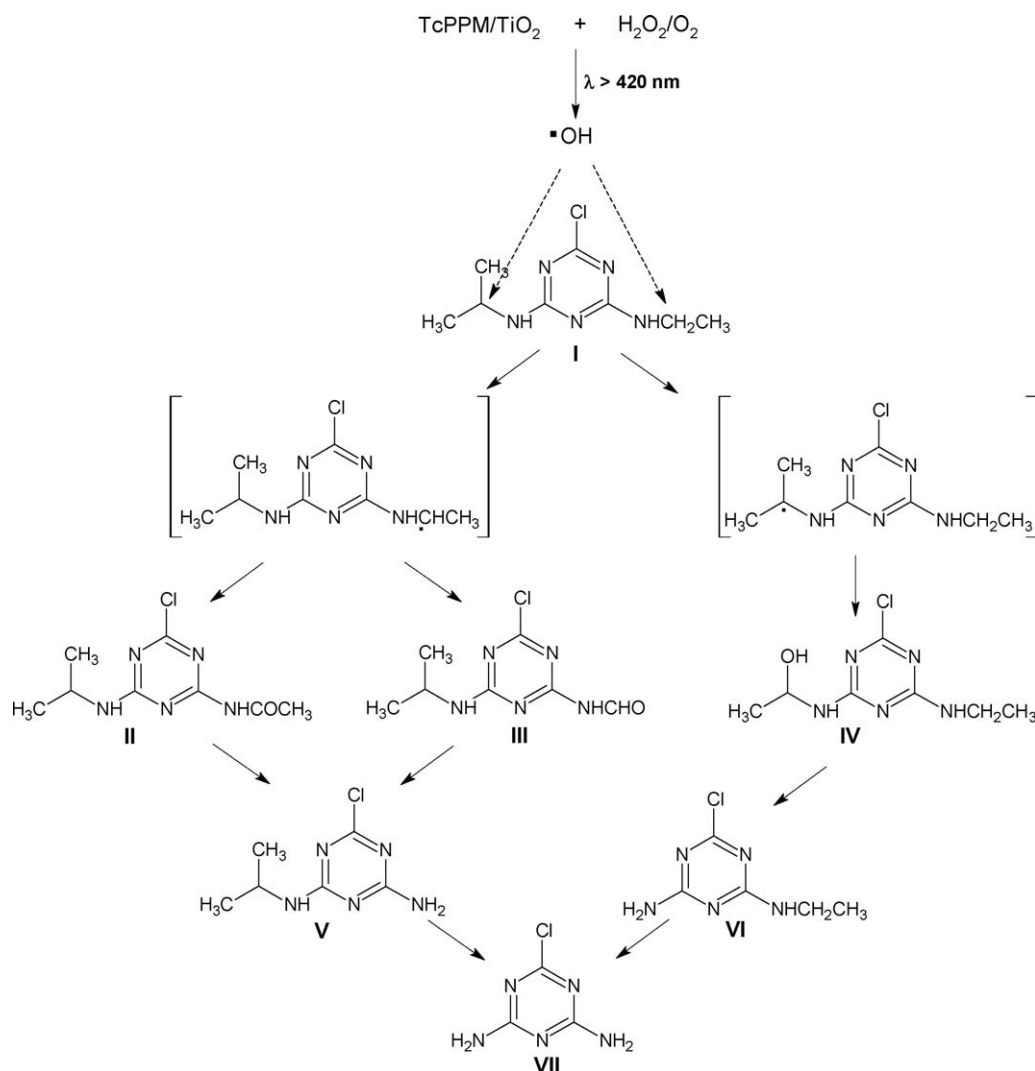


Fig. 7. Possible pathways for the formation of main intermediates of atrazine degradation with visible light irradiation.

A possible route for the generation of hydroxyl radicals is due to the fact that the hydrogen peroxide is shown to coordinate reversibly to Fe and Cu complexes, compared to Zn and metal-free porphyrins, bound to TiO_2 surface, according to the following

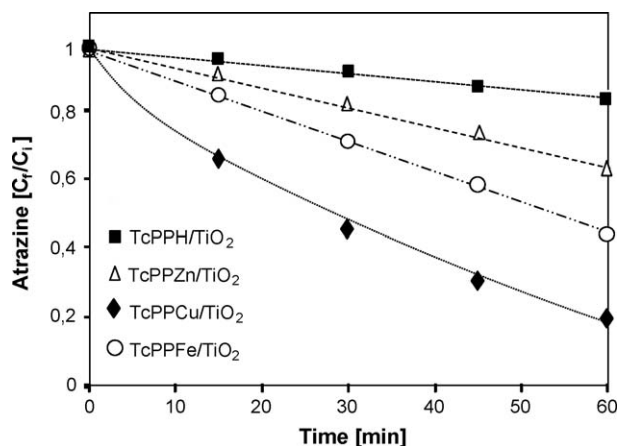
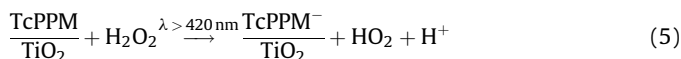


Fig. 8. Degradation of atrazine vs. irradiation time with Fe, Cu, Zn and metal-free porphyrins adsorbed on TiO_2 surface; in presence of O_2 and H_2O_2 . Experimental conditions: [atrazine] = 20 ppm; $[\text{H}_2\text{O}_2]$ = 0.05 M; catalyst charge = 1 g L^{-1} ; reaction volume = 20 mL, $I_0 = 1.1 \times 10^{-4} \text{ Einstein L}^{-1} \text{ s}^{-1}$; $\lambda > 420 \text{ nm}$.

reactions [60–62]:



Photoinduced oxidation of H_2O_2 by $\text{TcPPM}/\text{TiO}_2$ yields $\text{HO}_2\bullet$, whereas the reduced metal porphyrin (TcPPM^-) is oxidized by H_2O_2 via a dark process to generate $\bullet\text{OH}$ [63].

3.7. Stability of photocatalysts

Porphyrins adsorbed onto TiO_2 showed good stability under irradiation conditions. The absence of structural modifications was confirmed by analytical and spectral data.

The FT-IR analyses of $\text{TcPPM}/\text{TiO}_2$ (before irradiation) show the presence of strong carboxylate asymmetric $1630 \text{ cm}^{-1} \nu(-\text{COO}^-_{\text{as}})$ and symmetric $1384 \text{ cm}^{-1} \nu(-\text{COO}^-_{\text{s}})$ bands. This reveals that carboxylic acid groups are chemisorbed as carboxylates onto the TiO_2 surface [34,38,39]. At the end of the photocatalytic process, $\text{TcPPM}/\text{TiO}_2$ samples were isolated by centrifugation, washed with MeCN and dried. The IR spectra show the characteristic stretching modes of the porphyrin ring and carboxylate groups which indicate that the mode of adsorption of TcPPM to the surface is maintained. Moreover, adsorbed porphyrins could be quantita-

tively recovered from the TiO₂ surface by desorbing them at alkaline pH, and the intensities of Soret and Q bands did not show any sign of reduction. These results indicate that neither significant decomposition nor chemical modification of the adsorbed sensitizer took place at the end of the photocatalytic process. TcPPM/TiO₂ continued to maintain good photocatalytic activity after several cycles (six times) [20,39].

4. Conclusions

The photocatalytic activity of tetra(4-carboxyphenyl)porphyrin with different metal centers (Fe(III), Cu(II), Zn(II) and metal-free), adsorbed on TiO₂ surface has been studied by carrying out the photodegradation of atrazine in aqueous solution and under visible light irradiation. It has been found that anion superoxide is not sufficiently oxidant to degrade directly atrazine showing by this way, the limit of this treatment. We recall here that OH• also was not able to degrade all kind of molecules. However, if one wants to maintain the advantage of the degradation under visible light irradiation, it has been shown that the addition of an optimized concentration of hydrogen peroxide in the solution was possible. Under this condition, the photocatalytic activity increased in the following order: TcPPH < TcPPZn < TcPPFe < TcPPCu.

A general scheme of degradation was proposed, involving the oxidation and dealkylation of aminoalkyl groups of the side chains of the pesticide.

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